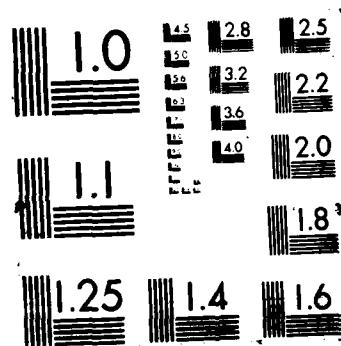


AD-A186 530 THE MECHANISM OF STEREO REGULATION DURING ANIONIC
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THE MECHANISM OF STEREO REGULATION DURING ANIONIC POLYMERIZATION OF
POLAR MONOMERS

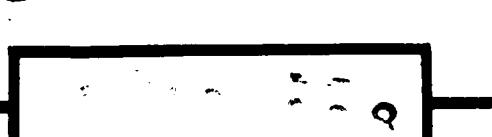
by

V.N. Krasulina, A.S. Khachaturov, et al.



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THE MECHANISM OF STEREO REGULATION DURING
ANIONIC POLYMERIZATION OF POLAR MONOMERS

By: V.N. Krasulina, A.S. Khachaturov, et al.

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| Block | Italic | Transliteration | Block | Italic | Transliteration |
|-------|--------|-----------------|-------|--------|-----------------|
| А а | А а | А, а | Р р | Р р | Р, р |
| Б б | Б б | В, б | С с | С с | С, с |
| В в | В в | В, в | Т т | Т т | Т, т |
| Г г | Г г | Г, г | У у | У у | У, у |
| Д д | Д д | Д, д | Ф ф | Ф ф | Ф, ф |
| Е е | Е е | Ye, ye; Е, е* | Х х | Х х | Kh, kh |
| Ж ж | Ж ж | Zh, zh | Ц ц | Ц ц | Ts, ts |
| З з | З з | Z, z | Ч ч | Ч ч | Ch, ch |
| И и | И и | I, i | Ш ш | Ш ш | Sh, sh |
| Й й | Й й | Y, y | Щ щ | Щ щ | Shch, shch |
| К к | К к | K, k | ѣ ѣ | ѣ ѣ | " |
| Л л | Л л | L, l | ѣ ѣ | ѣ ѣ | ѣ, є |
| М м | М м | M, m | ѣ ѣ | ѣ ѣ | ' |
| Н н | Н н | N, n | Э э | Ә ә | Е, е |
| Ӧ Ӧ | Ӧ Ӧ | Ӧ, Ӧ | Ӯ ю | Ӯ ю | Yu, yu |
| Ӧ Ӧ | Ӧ Ӧ | Ӧ, Ӧ | Я я | Я я | Ya, ya |

*ye initially, after vowels, and after b, b; e elsewhere. When written as є in Russian, transliterate as ѿ or є.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

| Russian | English | Russian | English | Russian | English |
|---------|---------|---------|---------|----------|--------------------|
| sin | sin | sh | sinh | arc sh | \sinh^{-1} |
| cos | cos | ch | cosh | arc ch | \cosh^{-1} |
| tg | tan | th | tanh | arc th | \tanh^{-1} |
| ctg | cot | cth | coth | arc cth | \coth^{-1} |
| sec | sec | sch | sech | arc sch | \sech^{-1} |
| cosec | csc | csch | csch | arc csch | csch^{-1} |

| Russian | English |
|---------|---------|
| rot | curl |
| lo | leg |

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THE MECHANISM OF STEREO REGULATION DURING ANIONIC POLYMERIZATION OF POLAR MONOMERS

V. N. Krasulina, A. S. Khachaturov, N. V. Mikhaylova, B. L. Yerusalimskiy

Formulation of the problem of the relative role of specific factors, which are basically capable of causing the corresponding effects, is justified in connection with the essential relationship of the micro structure of polymers, which are formed due to the action of anionic initiators, to the nature of the reaction medium. One of them is the change of overall polarity of the medium during the transition from one solvent to another, and the second is a formation of complexes of active reaction centers of growth with components of the medium, which have electron donor properties. In this report we shall limit our examination to the particular but very interesting case, specifically the system of the metal alcyi-polar monomer-non-polar solvent with the inclusion of data obtained in studying the microtactics of polymethylmethacrylic (PMMA), which is formed due to the action of lithium butyl with various ratios of monomer to solvent.

The affect of medium polarity, developed by the monomer itself, on the structure of polymers was not studied until recently; the overwhelming majority of information on relationship of the structure of macromolecules to nature of the reaction medium was obtained for systems with different hydrocarbon and polar solvents. An exception is data of Abbe and Smets [1] and the brief publication of Amerik and others [2] which appeared after completion of this work, where an increase of the isotactic consequences in PMMA was noted with a reduction of concentration of monomer during anionic polymerization in hydrocarbon medium; the mechanism of this phenomenon was not examined in particular. Similar results, which were derived by us for systems methylmethacrylic (MMA) - lithium butyl (LB) - toluene (interval of concentrations of monomers from 0.1 to 8.45 mole/l), were the bases for the system of stereo regulation in processes of anionic polymerization of the polar monomer.

The synthesized polymers were studied by infrared and NMR spectroscopy methods. The infrared spectra were used to determine stereo regularity of polymers for the value of the J factor, whose calculation is given in [3] (in accordance with [3] for isotactic polymer $J=25-35$, and for the syndiotactic polymer $J=100-115$). The NMR spectra were taken in the JNM-4N-100 spectrometer with working frequency of 100 MHz $100-110^\circ$, and also at room temperature. The samples were dissolved in tetrachloroethylene (concentration about 7%), as a standard we used tetramethylsilane. The table gives conditions of

polymerization and spectro characteristics (the J factor for data of the infrared spectra in fractions of the iso-hetero and syndiotactic triads (ii, si, ss), which are derived from areas of NMR lines of absorption of the alpha-methylene groups) for all polymers.

The Affect of Concentration of Monomer on the Micro Structure of Polymers. Which are Formed in the System MMA-LB-Toluene

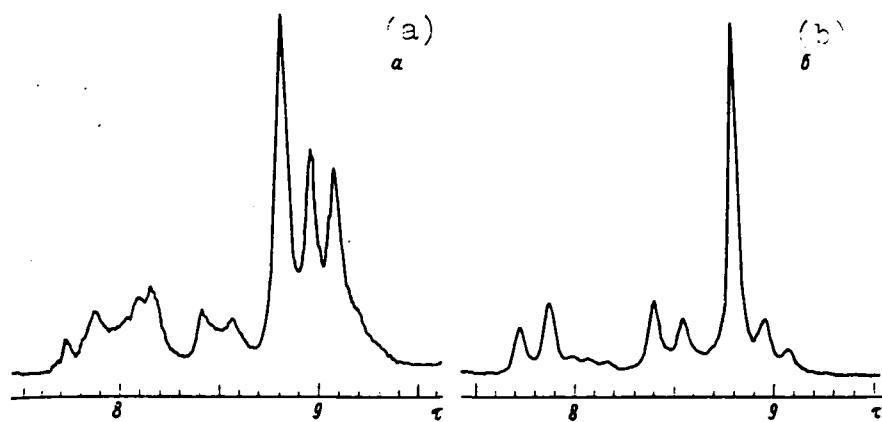
| Поли- мер, № | Концентрация, моль/л | | Темпера- тура, °C | Фактор J | Триады, % | | | (10) |
|-----------------|-------------------------|-----------|----------------------|----------|-----------|-----|-----|------|
| | моно- мер | инициатор | | | (2) | (3) | (4) | |
| 1 | 8.45 | 0.045 | -50 | 66 | 52 | 25 | 23 | |
| 2 | 0.86 | 0.040 | -50 | 38 | 75 | 16 | 9 | |
| 3 | 0.1 | 0.012 | -50 | — | 71 | 17 | 12 | |
| 4 | 0.55 | 0.020 | -60 | 35 | 80 | 13 | 7 | |
| 5 | 4.7 | 0.020 | -70 | 62 | 45 | 25 | 30 | |
| 6 | 0.21 | 0.020 | -70 | 35 | 77 | 14 | 9 | |

Key: (1) Polymer, No.; (2) Concentration, moles/l; (3) Monomers; (4) Initiators; (5) Temperature, °C; (6) J factors; (7) Triads, %; (8) Iso-; (9) Hetero-; (10) Syndio.

The figure presents NMR spectra for samples 5 and 6 (range of absorption of methylene and alpha-methylprotons). The lines with 8.78, 8.95 and 9.09 pertain to alpha-methyl groups in the triads ii, is and ss respectively. The absorption lines of the methylene groups, calculated for 100 MHz, are located respectively in the following tetrads: sss (the singlet with τ 8.15); isi (singlet with τ 8.02); iii and sis (quartet with τ 7.71; 7.86; 8.40; 8.55); iis (quartet with τ 7.81; 7.96; 8.47; 8.62); iss (the quartet with τ 7.92; 8.07; 8.10; 8.25). Coupling of the established quantities leads to a conclusion on the greatest uniformity of the chain for the case of polymers, which are produced with low concentration of monomers; macromolecules, which

are formed under these conditions, differ in maximal content of isotactic sequences; the specific weight of the hetero-triad (that is departures from regularity) is quite small, which is indicative of the large lengths of the dominating isotactic stereo blocks. The distinct quartet of the absorption line of the methylene protons is indicative of this (see the figure). The increase concentration of monomer encourages an increase of the relative content of syndiotactic sequences, but the isotactic lengths remain dominate; this is evidenced by the great intensity of the peak of the alpha-methyl group in the isotactic triads, as well as by preservation of the quartet for the methylene group.

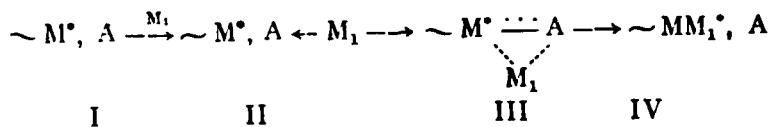
Analysis of the ratio of intensities of components of methylene and methyl lines [4] for polymers, which are given in the figure, allows one to establish that the average length of the isotactic sequence in the polymer 6 is 10 monomer lengths, and for the syndiotactic it is 2 lengths. For polymer No. 5 similar average lengths are 4 and 2 lengths respectively.



NMR spectra of samples of PMMA: a is 5 and b is 6 (see the table), taken at a frequency of 100 MHz at 107 and 112° respectively.

The NMR spectra at 100 MHz allow one to discover an even more remote interaction, absorption lines of the methylene groups are sensitive not only to structures of dyads, but also of tetrads [5]. Thus, for the sample 6 presented in the figure the overwhelming part of the methylene lines pertains to tetrads iii (above 80%). Of the remaining fraction approximately 40% are for tetrads iss and 30% each for tetrads sss and isi. In sample 5 the fraction of tetrads, which include the syndiotactic configurations, increases greatly (up to about 45%). Among them the greater part is for the sss tetrads, they are above 40% (or approximately 18% of the total number). 30% is for the tetrads iss, and the remaining for the tetrads isi (approximately 13%) and iis (approximately 17%). A portion of the syndioconfigurations is attributed to the tetrads sis, the quartet of which is indistinguishable from the quartet for iii.

Thus, the general nature of the relationship of the structure of macromolecules to concentration of monomer is in accordance with the well known data on the predominate formation of isotactic PMMA in hydrocarbon solvents and syndiotactic in the polar solvents [6-8]. Never the less, interpretation of the revealed relationship as a function of polarity of the medium is not the uniquely possible one. Another view point is possible, which is based on the representation of the progress of the reaction of growth through the stage of complex formation of monomer with active center approximately M^* , A (where A is a anti ion) according to the type

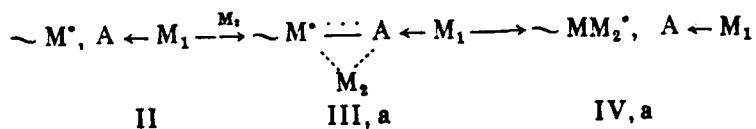


It is most probable that the formation of isotactic sequences is caused by specific orientation of the monomer within the complex II. On the other hand, the syndiotactic construction of specific segments of the polymer chain can be represented as a result of the growth according to the scheme

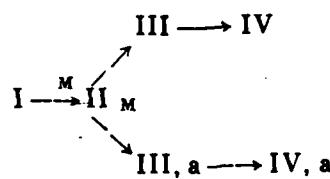


that is in addition to the stage of the formation of complex II. An exception or reduction of relative role of this stage can be cause by different factors. Within in our examination the basic possibility of the competition of the acts of the transition $II \rightarrow III$ and interaction of the complex II with the new molecule of the monomer (M_2) with preservation of the proceeding one (M_1) in the coordination sphere of

the anion is deserving of attention:



The parallel course of the growth reaction for both paths is formulated by the following scheme, in which the directions (1) and (2) symbolize the formation of the iso- and syndiotactic sequences respectively:



In contrast to direction (1), for which the formation stage of the complex II can not be kinetically determining for the growth reaction, direction (2) should depend on the concentration of monomer. This can be explained by the affect of concentration of monomer on the micro structure of a polymer, if one considers the direction (1) optimal for the isotactic construction of the chain.

These considerations are in agreement with the high sensitivity of structure of polymers, which are formed in anion systems, to the presence of negligible quantities of Lewis bases (see, for example [1]). The introduction of small portions of these agents practically has no affect on the overall polarity of the reaction medium, therefore the observed effects should be attributed to blocking of the anti ion by these compounds, that is to the partial or complete elimination of the formation of complexes II. This hypothesis, evidently, was first formulated by Bywater [9] and some what developed in a review article

[10], of course it does not eliminate the generally accepted considerations of the affect of the nature of the medium on parameters of the active bond of the growing chain. In the general case it is difficult to separate both factors, but with respect to systems with low concentration of additional polar agents a critical role of the elimination of the formation stage of complex II is completely justified.

Conclusions

1. The content of isotactic sequences in polymers, which are formed in the system methylmethacrylate-lithium butyl-toluene at low temperature, increases with reduction of monomer concentration.

2. It is suggested that this phenomenon is caused by competition of the reactions of growth, which occur through the stage of formation of the monomer complex with the anti ion and along side it.

Submitted
April 2, 1969

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